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cold flame originates, remain unchanged to the very end of the reaction, while the amount of peroxides sharply decreases during this last stage of oxidation. The accumulation of the other reaction products continues without any interruption throughout the course of the entire cold-flame oxidation. Note that the rate of increase in CO during each cold-flame period is significantly greater than that during the intervals between the flames.

It is interesting to note that, after a number of experiments have been run, a white, powdery coating forms on the cold connecting parts of the apparatus near the reaction vessel. This coating can be removed by careful heating with an alcohol burner and simultaneous evacuation with a pump.

Comparison of these results with those obtained in the investigation of the high-temperature oxidation of propane [1] leads to the conclusion that the chemistry of the oxidation of propane in both temperature ranges is very similar. In both cases, the total process of oxidation of propane consists of its actual oxidation and its cracking. For example, in the high-temperature oxidation of the mixture  $C_3H_8 + O_2$  at the end of the reaction taking place at  $350^\circ$ , the ratio of propane consumed in the oxidation to the propane cracked is 0.65.[3]

This ratio for the same mixture in the present work on the cold-flame reaction was found to be 0.46. A decrease in the ratio is perfectly natural, since a decrease in temperature (in changing over to cold-flame oxidation) has a greater effect on the cracking than on the oxidation. The products (including the peroxides) of both phases [oxidation and cracking] of high-temperature and cold-flame oxidation are identical.

Furthermore, in the change from high-temperature to cold-flame oxidation of propane, there is no significant change in the quantitative relationship of reaction products. This is shown to be true by the data in Table 2 [appended], which correspond to the moment at the end of the reaction.

In investigating the high-temperature oxidation of propane ( $C_3H_8 + O_2$ ,  $T = 350^\circ$ ,  $P_{initial} = 282$  mm), it was found that the maximum velocity, as calculated from the increment in pressure, occurs at the moment when  $\Delta p = 17$  mm. Constant concentration of aldehydes and maximum concentration of peroxides are established at a later moment of the reaction, when  $\Delta p = 30$  mm. If there is really a congruence of chemical processes over the entire range of slow oxidation of hydrocarbons, then in the case of cold-flame oxidation of propane one can expect a similar congruence of the moment of maximum velocity, as calculated from the pressure increment, with the moment when the concentration of aldehydes becomes constant and the concentration of peroxides reaches a maximum.

Our data support this hypothesis. As we saw above, the maximum velocity of cold-flame oxidation, as calculated from the pressure increment (after omitting the peaks), occurs at the moment when  $\Delta p = 15$  mm; when  $\Delta p = 50$  mm, the concentration of aldehydes becomes constant and the concentration of peroxides reaches a maximum (see Figure 3). This, undoubtedly, is an additional confirmation of the hypothesis that the same chemical processes comprise the basis for both high-temperature and cold-flame oxidation of propane.

From this point of view, cold-flame flashes merely represent insignificant side reactions and do not give rise to a measurable formation and accumulation of aldehydes and peroxides. Our results are in good agreement with this hypothesis of the nature of cold flames. In fact, as shown above,

- 2 -

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

aldehydes and peroxides accumulate only during the occurrence of cold flames which are superimposed on the basic chemical process in that part of it where the maximum quantity of these products has not yet formed (first and second cold flames). However, if the cold flame originates after this moment, as for example the third cold flame does, it can no longer produce an additional accumulation of aldehydes and peroxides.

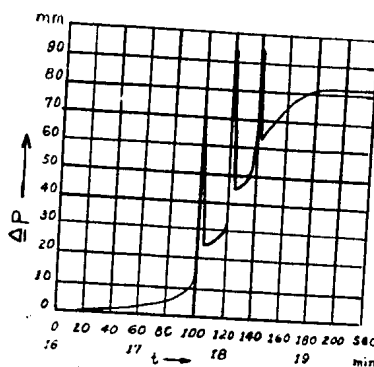


Figure 1. Kinetic curve ( $\Delta p - 1$ ) of cold-flame oxidation of the mixture  $C_3H_8 + O_2$ ;  $T = 280^\circ$ ;  $P_{initial} = 420$  mm

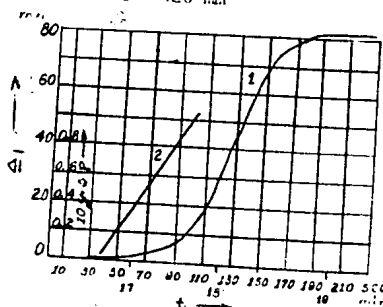


Figure 2. Kinetic curve of change of pressure in cold-flame oxidation of propane after omission of peaks (1) and its semilogarithmic anamorphosis (2). Mixture of  $C_3H_8 + O_2$ ;  $T = 280^\circ$ ;  $P_{initial} = 420$  mm

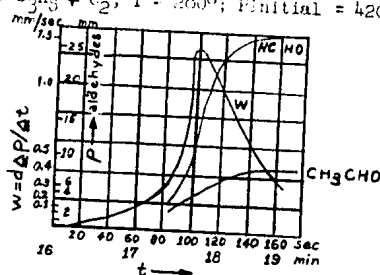


Figure 3. Rate of change of pressure (curve  $w$ ) and of the concentrations of aldehydes (curves  $HCHO$  and  $CH_3CHO$ ) during course of cold-flame oxidation of mixture  $C_3H_8 + O_2$ ;  $T = 280^\circ$ ;  $P_{initial} = 420$  mm

- 3 -

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Table 1. Analysis of the Mixture  $C_3H_8 + O_2$  During the Course of Cold-Flame  
Oxidation:  $T = 32^\circ C$ ;  $P_{initial} = 420$  mm (case of three cold flames)

Moment of Reaction	Composition of Mixture (mm)										
	$HCHO$	$CH_3CHO$	Peroxides*	$CH_3OH$	Acids	$C_2H_4$	$C_2H_6$	$H_2$	$CO$	$CO_2$	$O_2$
17 min, 24 sec	4.3	2.8	1.8	9.2	3	--	--	--	--	--	--
17 min, 39 sec	8.9	4.7	4.5	15.6	3.6	--	--	--	--	--	--
Before 1st cold flame	12.5	6.9	8.4	17.7	6.1	1.1	3.5	3.4	13.9	6.0	163.0
End of " " "	16.1	9.1	11.1	25.0	3.3	1.0	5.0	3.0	24.0	0.05	145.0
Before 2d " "	20.9	6.0	3.7	34.0	5.3	1.5	6.7	5.1	31.5	11.6	125.0
End of " " "	24.1	7.4	2.0	30.0	4.3	17.1	8.0	6.4	52.5	13.4	92.0
Before 3d " "	27.0	7.4	1.73	31.0	5.4	15.9	11.0	6.2	60.5	19.6	67.0
End of " " "	27.9	7.05	1.4	42.4	5.0	21.0	11.6	7.1	74.0	22.0	51.0
End of reaction	26.5	3.0	1.1	49.0	3.4	17.3	13.0	0.5	100.0	27.0	12.5

\* The peroxides consisted of approximately 70%  $H_2O_2$  and 30% organic peroxides, as found by polarographic and chemical analysis.

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Table 2. Reaction Product Ratios

	High-Temperature Oxidation*	Cold-Flame Oxidation
$\frac{\text{HCHO}}{\text{CH}_3\text{CHO}}$	2.6	3.0
$\frac{\text{CH}_3\text{CHO}}{\text{CH}_3\text{COH}}$	1.5	0.4
$\frac{\text{CH}_3\text{CHO}}{\text{HCHO} + \text{CH}_3\text{COH}}$	1.4	1.1
$\frac{\text{C}_2\text{H}_6}{\text{C}_2\text{H}_4}$	0.5	1.7
$\frac{\text{CO} + \text{CO}_2}{\text{O}_2 \text{ spent}}$	0.69	0.67

\* Analytical data obtained in the oxidation of the mixture  $\text{C}_2\text{H}_6 + \text{O}_2$  at  $T = 350^\circ$  and pressure 1 atm. (see also [1] for the calculation of the ratios [1]).

## BIBLIOGRAPHY

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